

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

Chains, Rings and Spectroscopy



2814

Monday

23 JANUARY 2006

Morning

1 hour 30 minutes

Candidates answer on the question paper.

Additional materials:

Data Sheet for Chemistry

Scientific calculator

Candidate
Name

Centre
Number

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Candidate
Number

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TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers, in blue or black ink, in the spaces provided on the question paper.
- Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure you know what you have to do before starting your answer.
- Do not write in the bar code. Do not write in the grey area between the pages.
- **DO NOT WRITE IN THE AREA OUTSIDE THE BOX BORDERING EACH PAGE. ANY WRITING IN THIS AREA WILL NOT BE MARKED.**

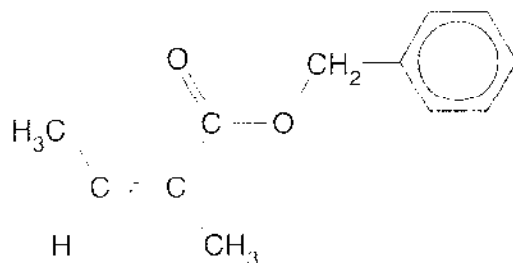
INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	12	
2	14	
3	13	
4	17	
5	10	
6	13	
7	11	
TOTAL		

Answer **all** the questions.

- 1 Compound **A** is used to add the flavour of mushrooms to foods.



compound **A**

- (a) (i) Apart from the benzene ring, name the two functional groups in compound **A**.

..... [2]

- (ii) Draw the skeletal formula of compound **A**.

[1]

- (iii) Deduce the molecular formula of compound **A**.

..... [1]

- (b) Compound **B** is a stereoisomer of compound **A**.

Explain what is meant by the term *stereoisomerism*. Use compounds **A** and **B** to illustrate your answer.

.....

- (c) If the food is cooked for a long time, naturally occurring acids catalyse the hydrolysis of compound **A**.

Draw structures to show the **two** organic compounds formed by the acid hydrolysis of compound **A**.

[2]

- (d) The hydrolysis of compound **A** can be monitored by sampling the mixture at regular intervals, separating the components, and recording their infra-red spectra.

- (i) State **two** absorptions that would be expected in the infra-red spectrum of compound **A**, and identify the parts of the molecule responsible for each.

.....
.....
..... [2]

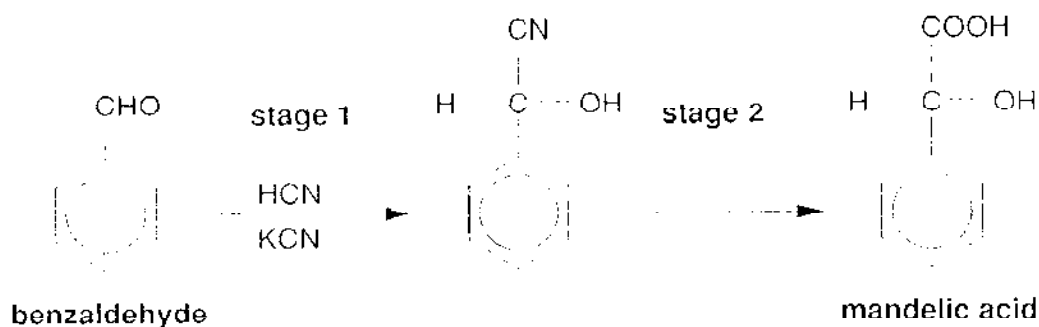
- (ii) Suggest a wavenumber range within the spectrum that could be used to clearly distinguish compound **A** from the products formed by the hydrolysis reaction.

Explain your answer.

.....
.....
.....
..... [2]

[Total: 12]

- 2 Mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, is found naturally in almonds. It is the active ingredient in some skin creams that are used to combat signs of ageing. Mandelic acid can be synthesised from benzaldehyde in two stages as shown below.



- (a) (i) Show in detail the mechanism for the reaction in **stage 1**.

[4]

- (ii) State the name of this mechanism.

[1]

- (b) Explain why reactions such as that used in **stage 1** are particularly useful in organic synthesis.

[1]

- (c) (i) State the reagents and conditions needed to carry out **stage 2**.

[2]

- (ii) Complete and balance the overall equation for the reaction in **stage 2**.



[1]

- (d) Explain why the mandelic acid produced naturally might be more effective as a drug than the same compound synthetically produced.

.....

.....

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.....

[3]

- (e) The compound made in stage 1, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CN}$, can be converted into another useful organic compound by reaction with LiAlH_4 in dry ether.

- (i) Identify the organic compound formed in this reaction.

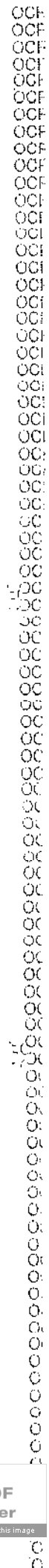
[1]

- (ii) State the type of reaction.

.....

[1]

[Total: 14]

[illegible][illegible][illegible]

- [illegible]

[illegible]

- [illegible]

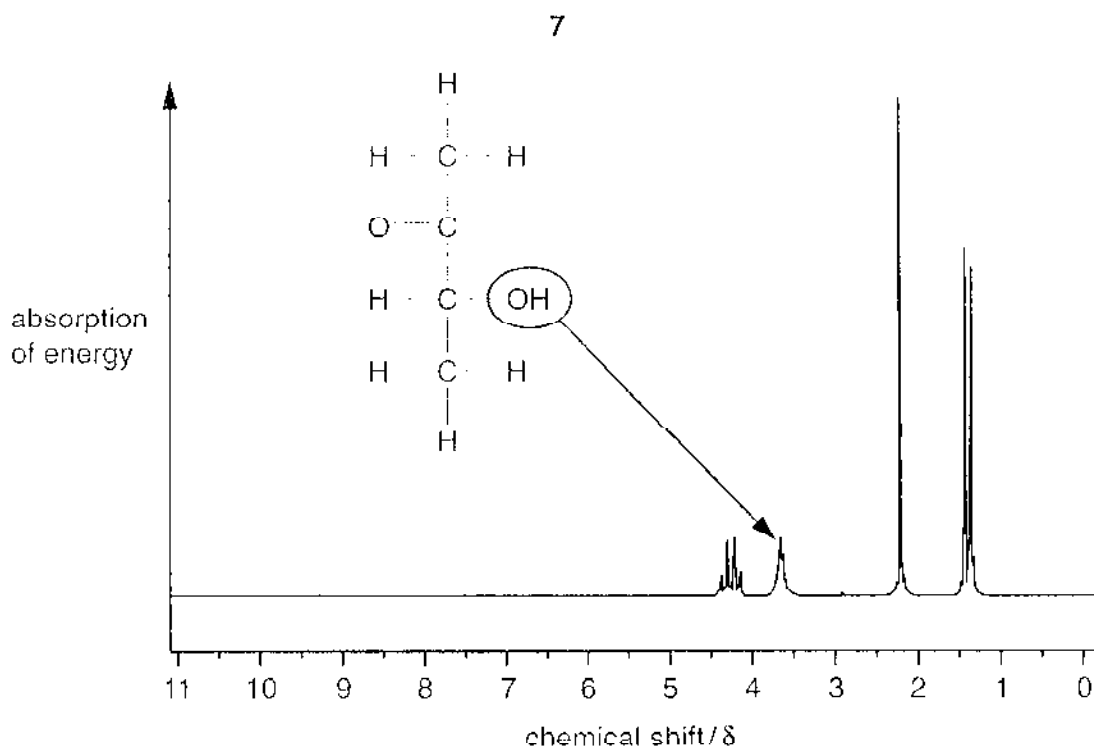
[illegible][illegible]

- [illegible]

- [illegible]

- [illegible]

[illegible]



n.m.r. spectrum of 3-hydroxybutanone

- (iii) Explain the splitting patterns shown by the peaks at $\delta = 1.4$ and $\delta = 4.3$.

.....

.....

.....

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.....

.....

[2]

- (iv) Underneath each of the four peaks on the spectrum above, write the relative peak area expected for that peak. [1]

- (v) What determines the relative area of a peak?

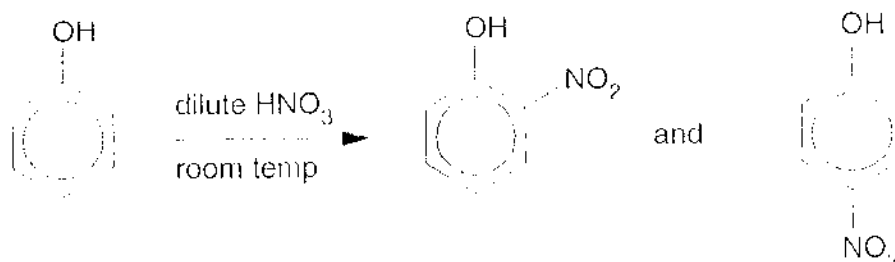
.....

.....

[1]

[Total: 13]

- 4 Phenol reacts readily with dilute nitric acid at room temperature in a nitration reaction to produce a mixture of products as shown below.



- (a) Suggest the structure of another organic product that is likely to be formed in the nitration of phenol.

[1]

- (b) Assuming a yield by mass of 27% for 4-nitrophenol, calculate the mass of 4-nitrophenol that would be produced from 100 g of phenol. Show your working.

Give your answer to an appropriate number of significant figures.

mass of 4-nitrophenol =

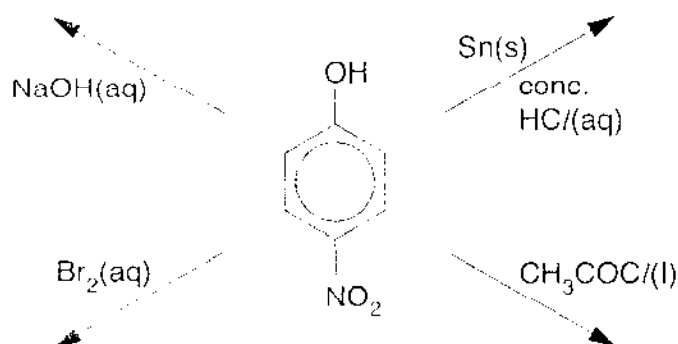
Compare the reagents and conditions for the nitration of phenol with those used for the nitration of **benzene**.

[7]

[7]

Quality of Written Communication [1]

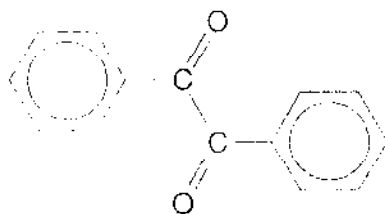
- (d) 4-Nitrophenol can be converted into a range of useful organic chemicals. Draw the structures of the organic products formed in the following reactions.



[4]

[Total: 17]

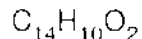
- 5 The reducing agent, NaBH₄, is used widely in organic chemistry. One example is for the reduction of diphenylethanedione, C₁₄H₁₀O₂, shown below.



diphenylethanedione

- (a) (i) Draw a displayed formula to show the structure of the organic product that would be formed by reducing diphenylethanedione with excess NaBH₄.

- (ii) Complete and balance the equation for this reaction, using [H] to represent the reducing agent.



[1]

- (b) Diphenylethanedione is a pale yellow colour, which disappears when it is reduced.

The colour results from the arrangement of the delocalised π -bond electrons.

Explain what is meant by the term *delocalised π -bond electrons*.

.....

.....

.....

..... [2]

- (c) Coloured organic compounds also include azo dyes.

Describe how an azo dye can be made from phenylamine. Show the structure of the azo dye and the organic intermediate in your answer.

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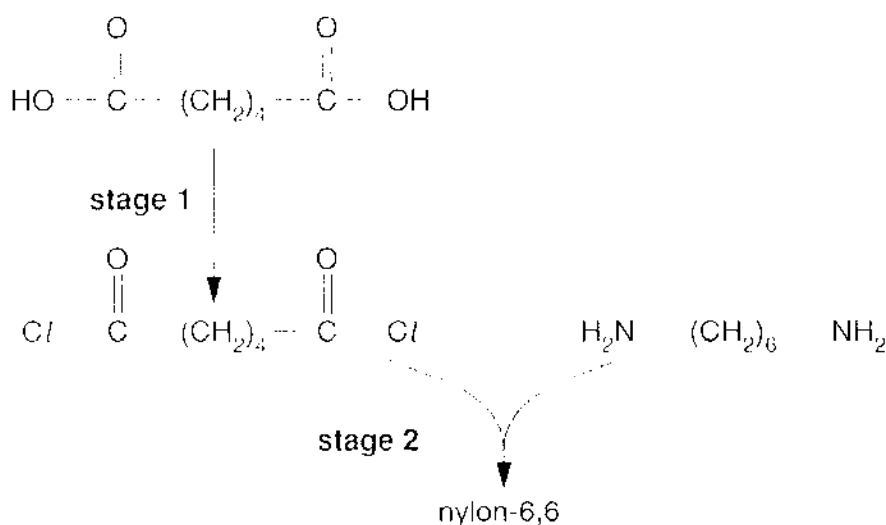
- 6 The fibres used in carpets are made from synthetic or natural polymers such as nylon-6,6, Orlon™ and wool.

(a) Complete the table below.

	nylon-6,6	Orlon™
monomer(s)	$\text{HO} - \overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_4 - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$ $\text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2$	
repeat unit of the polymer		$\begin{array}{ c c } \hline \text{H} & \text{CN} \\ \hline \text{C} & \text{C} \\ \hline \text{H} & \text{H} \\ \hline \end{array}$
type of polymerisation		

[4]

- (b) Nylon-6,6 can be made from its monomers in the laboratory in two stages as shown below.



- (i) State a suitable reagent to carry out **stage 1**.

[1]

- (ii) Deduce the inorganic product that is also formed in **stage 2**.

- (c) Industrially, nylon-6,6 is **not** manufactured by the method in (b). Instead, the two monomers are mixed directly at room temperature to give a salt. This salt is then heated to convert it to nylon-6,6.

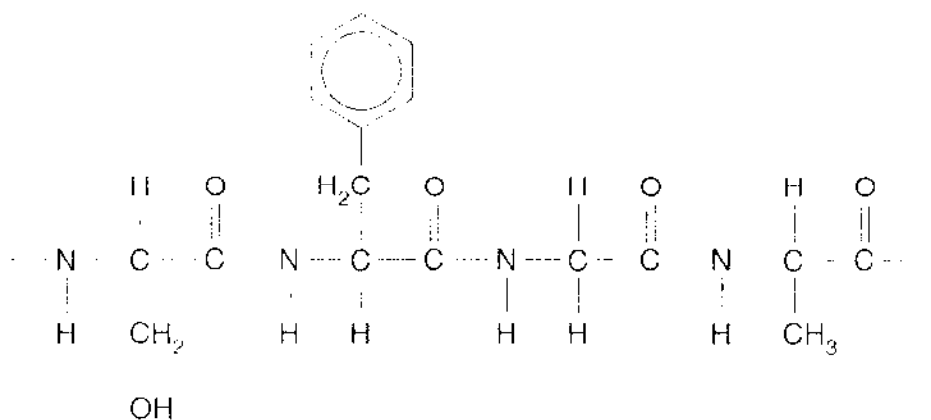
Suggest the structures of the two ions present in this salt.

[2]

QUESTION 6 CONTINUES ON THE NEXT PAGE

- (d) Wool is a protein. It is a natural polymer made by the same type of polymerisation as nylon-6,6.

A section of the polymer chain in a protein is shown below.



- (i) How many monomer units does this section contain? [1]
- (ii) Draw the structure of **one** of the monomer molecules that was used to form this section.

[1]

- (iii) State **three** ways in which the monomer units of a protein differ from those of nylon-6,6.

.....

.....

.....

.....

..... [3]

[Total: 13]

- 7 (a) In this question, one mark is available for the quality of use and organisation of technical terms.

Bromine is used in organic chemistry to carry out a variety of electrophilic reactions.

- (i) Describe and explain how a molecule of bromine acts as an electrophile. Illustrate your answer with a diagram showing relevant dipoles and curly arrows.
- (ii) Use your answer to (i) to explain why bromine reacts much more readily with cyclohexene than it does with benzene.

[7]

(b) The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction.

(i) Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.

.....

.....

.....

..... [2]

(ii) Deduce an equation for the reaction of iodine monobromide with benzene.

[1]

[Total: 11]

END OF QUESTION PAPER

Mark Scheme 2814

January 2006

ADVICE TO EXAMINERS ON THE ANNOTATION OF SCRIPTS

1. Please ensure that you use the **final** version of the Mark Scheme.
You are advised to destroy all draft versions.
2. Please mark all post-standardisation scripts in red ink. A tick (✓) should be used for each answer judged worthy of a mark. Ticks should be placed as close as possible to the point in the answer where the mark has been awarded. The number of ticks should be the same as the number of marks awarded. If two (or more) responses are required for one mark, use only one tick. Half marks should never be used.
3. The following annotations may be used in when marking. No comments should be written on scripts unless they relate directly to the mark scheme. Remember that scripts may be returned to centres.

<i>in</i>	=	incorrect response (errors may also be underlined)
<i>o</i>	=	omission of the correct response
<i>bot</i>	=	"benefit of the doubt" (where professional judgement has been used in deciding a response is worthy of a mark)
<i>ecf</i>	=	"error carried forward" (in consequential marking)
<i>con</i>	=	contradiction (in cases where candidates contradict themselves in the same response). No mark awarded, even if one response was correct. ¹
<i>sf</i>	=	error in the number of significant figures (only penalised once on the paper).
4. The marks awarded for each part question should be indicated in the margin provided on the right hand side of the page. The mark total for each question should be ringed at the end of the question, on the right hand side. These totals should be added up to give the final total on the front of the paper.
5. In cases where candidates are required to give a specific number of answers, (e.g. 'give three reasons ...'), mark the first answer(s) given up to the total number required. Strike through the remainder. In specific cases where this rule cannot be applied, the exact procedure to be used is given in the mark scheme
6. Correct answers to calculations should gain full credit even if no working is shown, unless otherwise indicated on the mark scheme. (An instruction to 'Show your working' is to help candidates, who may then gain partial credit even if their final answer is not correct.)
7. Strike through all blank spaces and/or pages in order to give clear indication that the whole of the script has been considered.
8. An element of professional judgement is required in the marking of any written paper, and candidates may not use the exact words that appear in the mark scheme. If the science is correct and answers the question, then the mark(s) should normally be credited. If you are in doubt about the validity of any answer, contact your Team Leader/Principal Examiner for guidance.

¹ Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

**Abbreviations,
annotations and
conventions used in the
mark scheme**

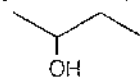
- / = alternative and acceptable answers for the same marking point
- : = separates marking points
- NOT = answers not worthy of credit
- () = words which are not essential to gain credit
- (underlining) = key words which **must** be used
- ecf = allow error carried forward in consequential marking
- AW = alternative wording
- ora = or reverse argument

**Marking structures in
organic chemistry**

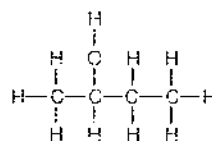
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3 , C_2H_5 , OH , COOH , COOCH_3) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient).

If not specified by the question, this may be given as either:

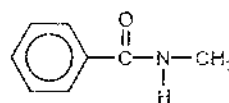
- a **structural formula** – e.g. $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$.



- a **skeletal formula** – e.g.



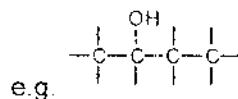
- a **displayed formula** – e.g.



or as a hybrid of these – e.g.

The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –



Benzene rings may be represented as



as well as

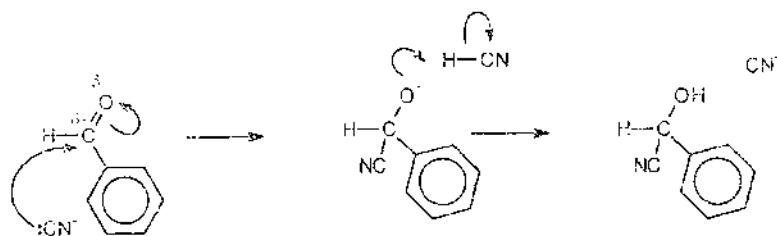


in any

of the types of formula above.

7. (a) (i)	alkene ✓ ester ✓	allow "C=C double bond"	[2]
1.		✓	[1]
ii.	$C_{12}H_{14}O_2$ ✓		[1]
b.	same structural formula/order of bonds, different spatial arrangement AW ✓		
	description or diagram showing B and how it is different from A ✓		[2]
c.		✓	[2]
c. i.	peak at 1680-1750 (cm^{-1}) due to C=O ✓		
	peak at 1000-1300 (cm^{-1}) due to C-O / ✓		[2]
ii.	2500-3300 / 3230-3550 (cm^{-1}) ✓		
	O-H / carboxylic acid / alcohol is <i>not</i> present in A ✓		
	allow 1 mark for ~500-1500 (cm^{-1}) which is a unique fingerprint region etc		[2]
			[Total: 12]

2 (a) (i)



polarisation of $C^{\delta-}=O^{\delta+}$ and curly arrow breaking $C=O$ ✓

curly arrow from lone pair on $:CN^-$ to C ✓

structure of intermediate ✓

curly arrows from O^- to $H-CN/H_2O$ and
breaking the $H-CN/H-OH$ bond ✓

allow just a curly
arrow from from
 O^- to H

[4]

iii. nucleophilic addition ✓

[1]

e. lengthening the carbon chain AW ✓

[1]

f. i. heat/reflux with a suitable strong acid /acid / H^+ ✓
which is dilute / (aq) / stated concentration ✓

allow 'conc' for HCl

[2]

ii. $C_6H_5CH(OH)CN + 2H_2O + H^+ \rightarrow C_6H_5CH(OH)COOH + NH_4^+$ ✓

[1]

g. mandelic acid is chiral / has optical isomers / enantiomers ✓

synthetic gives a mixture / natural gives only one (optical) isomer ✓

only one of the (optical) isomers is the (pharmacologically) active
one AW ✓

ignore references to
side effects and
dosage

[3]

h. i. $C_6H_5CH(OH)CH_2NH_2$ / 2-amino-1-phenylethanol
any unambiguous formula/name ✓

[1]

ii. reduction / redox ✓

[1]

[Total: 14]

3 (c) low boiling point / easily turns to a gas AW ✓ [1]

i. 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent ✓

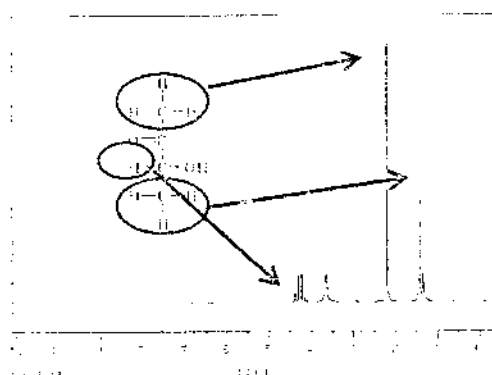
purify/recrystallise the product/solid (derivative) ✓

measure the melting point /mp ✓

compare the result with data book/known values ✓

[4]

ii.



one mark for two peaks assigned ✓

two marks for all three ✓

[2]

iii. re-run in/add D₂O ✓

peak (due to OH) disappears ✓

[2]

iii. Peak at 1.4ppm

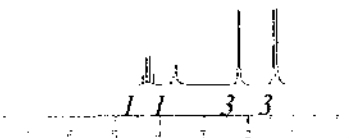
(1:1 due to) one H on the neighbouring /adjacent carbon ✓

Peak at 4.3ppm

(1:3:3:1 due to) three H on the neighbouring /adjacent carbon ✓

[2]

iv.



all four correct ✓

[1]

v. no of H/protons in the same (chemical) environment/of that 'type' ✓

[1]

[Total: 13]

4 (a) Correct structure of 3-nitrophenol or any multiple nitrated phenol ✓ [1]

k. M_r phenol (C_6H_6O) = 94.0 ✓

M_r 4-nitrophenol ($C_6H_5NO_3$) = 139.0 ✓

expected mass/moles of nitrophenol from 100 g =

148 g/1.06 mol (or ecf from wrong M_r s) ✓

at 27% yield gives 40 / 39.9 (g) (or ecf) ✓

last mark is for 0.27 x

expected mass to 2 or 3 sf [4]

l. conditions for nitration of benzene:

HNO_3 is concentrated ✓

conc H_2SO_4 is present ✓

heating or stated temp above $50^\circ C$ ✓

[3]

explanation for greater reactivity of phenol

lone pair from O atom is delocalised into the ring ✓

greater (π) electron density around the ring ✓

(the benzene ring in phenol) is activated ✓

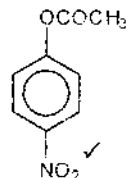
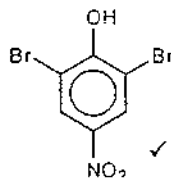
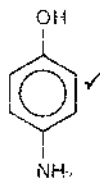
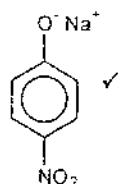
attracts electrophiles/ NO_2 more / makes it more susceptible to electrophiles AW ✓

[4]

quality of Written Communication mark for at least two legible sentences with correct spelling, punctuation and grammar

[1]

m.

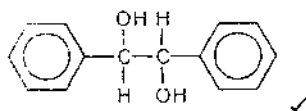


allow bromination in any positions on the ring

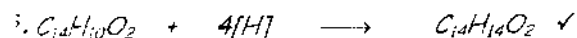
[4]

[Total: 17]

b (4) (5)



[1]



allowed from (i)

[1]

(i) *delocalised electrons*

electrons are spread over more than two atoms AW ✓

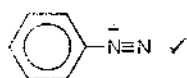
π-bond

formed by overlap of p-orbitals/ diagram to show ✓

[2]

(ii) *sodium nitrite + HCl / nitrous acid* ✓

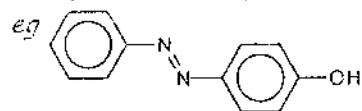
40°C ✓



phenol/named example (added to the products from above) AW ✓

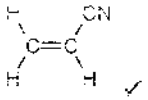
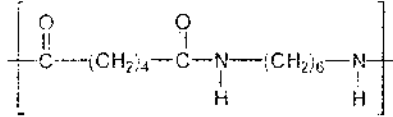
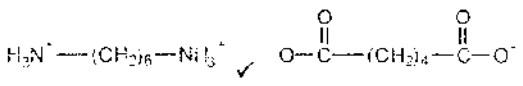
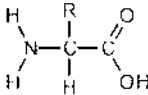
alkaline conditions / OH ✓

example of an azo dye that could be formed from phenylamine,



[6]

[Total: 10]

6 (a)	<div style="text-align: center;">  </div> <div style="text-align: center;">  <p><i>monomers connected by NHCO ✓</i> <i>correct repeat shown ✓</i></p> <div style="display: flex; justify-content: space-around; width: 100%;"> condensation addition </div> </div>	✓ for both	[4]
p. i. $PCl_5 / SOCl_2$			[1]
ii. HCl			[1]
q.	<div style="text-align: center;">  </div> <p><i>allow 1 mark for: both $H_3N^+-(CH_2)_6-NH_2$ and $HO-C(=O)-(CH_2)_4-C(=O)-O^-$</i></p>		[2]
r. i. 4			[1]
ii.	<div style="text-align: center;">  <p><i>where R = H, CH₃, CH₂OH or CH₂C₆H₅ ✓</i></p> </div>		[1]
iii. any three different chemically or biologically correct differences between amino acids and the nylon monomers ✓✓✓ - eg			
<ul style="list-style-type: none"> protein monomers are amino acids / nylon monomers are a (di)amine/base and a (di)acid protein monomers have different types/R groups / nylon monomers are two types/no variation protein monomers have stereo/optical isomers/are chiral protein monomers have higher melting points/form zwitterions 			
other possible answers include:			
<ul style="list-style-type: none"> nylon monomers have longer chain length/no other functional groups / no aromatic content / are symmetrical etc 			
<i>don't allow comparisons of solubility or M_r</i>			
[Total: 13]			

7 (c) (i) bromine as an electrophile

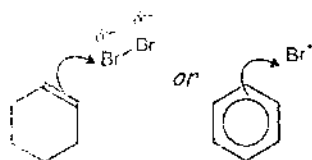
an electrophile accepts an electron pair ✓

NOT a lone pair

Bromine is polarised/has + charge (centre)/dipole on Br-Br/Br⁺ shown in diagram ✓

appropriate diagram showing a curly arrow from a double/ π bond to the Br⁺/Br⁺ ✓

eg



[3]

iv. comparison of reactivity of cyclohexene and benzene

benzene is (more) stable / more energy required ✓

benzene (π) electrons are delocalised ✓

benzene has lower electron/- charge density ✓

so bromine is less polarised / attracted to it /

benzene is less susceptible to electrophiles ✓

o.s. for cyclohexene

[4]

quality of written communication mark for any two of the the terms:

delocalised/localised, π -electrons/bonds/system, electron density,
 dative covalent, activation/stabilisation energy, halogen carrier,
 heterolytic fission, addition/substitution, polarity used appropriately ✓

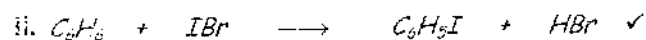
[1]

c. i. iodobenzene because ...

Br is more electronegative than I ✓ ora

so the I atom will be positive / δ^+ /the electrophile ✓

[2]



or ecf giving $C_6H_5Br + HI$

[1]

[Total: 11]